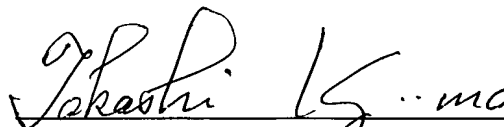




C E R T I F I C A T I O N

I, Takashi KOJIMA of Ginza Ohtsuka Bldg., 2F, 16-12, Ginza 2-chome, Chuo-ku, Tokyo, Japan, hereby certify that I am the translator of the accompanying certified official copy of the documents in respect of an application for a patent filed in Japan on the 4th of February, 2000 and of the official certificate attached thereto, and certify that the following is a true and correct translation to the best of my knowledge and belief.

Dated this 7th day of June, 2004


Takashi KOJIMA

(Translation)



PATENT OFFICE
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This is to certify that the annexed is a true copy of the following application as filed with this Office.

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Application Number: Japanese Patent Application
No. 2000-027713

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Seisakusho

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Commissioner,
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Kozo OIKAWA
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[List of Documents Attached]
[Document] Specification 1
[Document] Abstract 1

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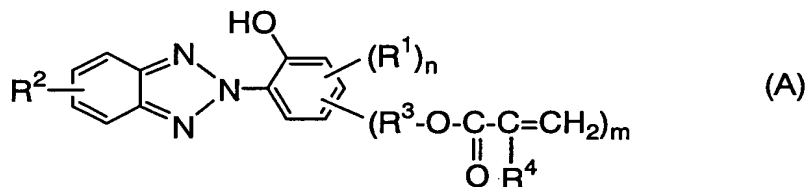
[SPECIFICATION]

[TITLE OF THE INVENTION] Coating Composition, Coating
Method, and Coated Article

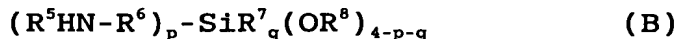
5 [CLAIMS]

[Claim 1] A coating composition comprising the reaction product of a benzotriazole compound having a polymerizable vinyl group and a hydroxyl group with a silane compound and/or a (partial) hydrolyzate thereof.

10 [Claim 2] The coating composition of claim 1 wherein the reaction product and/or (partial) hydrolyzate is the reaction product obtained by effecting addition reaction between a compound of the general formula (A):



wherein R¹ and R² each are hydrogen, a halogen atom or alkyl group of 1 to 10 carbon atoms, R³ is a substituted or
15 unsubstituted divalent hydrocarbon group of 1 to 18 carbon atoms, R⁴ is hydrogen or an alkyl group of 1 to 4 carbon atoms, n is an integer of 0 to 2, and m is an integer of 1 to 3, and an amino group-containing organoxysilane of the
20 general formula (B):



wherein R⁵ is hydrogen or an alkyl group of 1 to 15 carbon
25 atoms, R⁶ is a divalent hydrocarbon group of 1 to 15 carbon atoms or an amino group-containing divalent hydrocarbon group of 1 to 15 carbon atoms, R⁷ is an alkyl group or aryl group of 1 to 10 carbon atoms, R⁸ is hydrogen or a monovalent organic group of 1 to 10 carbon atoms, p is equal to 1 or 2,
30 q is equal to 0 or 1, and p+q is equal to 1 or 2, and/or a (partial) hydrolyzate thereof.

[Claim 3] The coating composition of claim 1 or 2 comprising

(1) 0.1 to 100 parts by weight of the reaction product of a benzotriazole compound having a polymerizable vinyl group and a hydroxyl group with a silane compound and/or a (partial) hydrolyzate thereof, and

(2) 100 parts by weight of a silane compound of the general formula (C):



wherein R^9 is an alkyl group, aryl group, halogenated alkyl group, halogenated aryl group or alkenyl group of 1 to 10 carbon atoms, or an organic group having an epoxy, (meth)acryloxy, mercapto, amino or cyano group, R^7 is an alkyl group or aryl group of 1 to 10 carbon atoms, R^8 is hydrogen or a monovalent organic group of 1 to 10 carbon atoms, r and s each are equal to 0, 1 or 2, and r+s is equal to 0, 1 or 2, and/or a hydrolyzate thereof.

20 [Claim 4] The coating composition of claim 1 or 2 comprising a co-hydrolyzate obtained by subjecting to co-hydrolysis (1) 0.1 to 100 parts by weight of the reaction product of a benzotriazole compound having a polymerizable vinyl group and a hydroxyl group with a silane compound and/or (partial) hydrolyzate thereof, and (2) 100 parts by weight of the silane compound of the general formula (C) and/or hydrolyzate thereof.

30 [Claim 5] The coating composition of any one of claims 1 to 4, further comprising (3) a microparticulate inorganic oxide containing at least one atom selected from titanium, cerium and zinc and capable of absorbing light having a wavelength of up to 400 nm.

[Claim 6] The coating composition of any one of claims 1 to 5, further comprising (4) colloidal silica.

35 [Claim 7] An article having a protective coating with improved weather resistance and abrasion resistance, the coating being formed from the coating composition of any one of claims 1 to 6.

[Claim 8] A primer coating composition comprising

(1) 0.1 to 50 parts by weight of the reaction product and/or (partial) hydrolyzate thereof set forth in claim 1 or 2, and

5 (5) 100 parts by weight of an organic copolymer of an acrylic and/or vinyl monomer containing an alkoxysilyl group with another monomer copolymerizable therewith, the acrylic and/or vinyl monomer containing an alkoxysilyl group accounting for 0.1 to 50% by weight of the copolymer.

10 [Claim 9] The primer coating composition of claim 8, further comprising 0.1 to 50 parts by weight of a compound containing a nitrogen atom and an alkoxysilyl group in one molecule.

[Claim 10] The primer coating composition of claim 9
15 wherein the compound containing a nitrogen atom and an alkoxysilyl group in one molecule is a compound containing at least one nitrogen atom and at least two alkoxysilyl groups in one molecule.

[Claim 11] The primer coating composition of any one of
20 claims 8 to 10, further comprising 0.1 to 10 parts by weight of a photo-stabilizer having at least one cyclic hindered amine structure in a molecule.

[Claim 12] A method for providing a plastic substrate with a weather resistant, abrasion resistant coating,
25 comprising the steps of:

(i) applying an organic solvent solution of the primer coating composition of any one of claims 8 to 11 onto a plastic substrate,

30 (ii) evaporating the organic solvent and curing the primer coating,

(iii) applying the coating composition of any one of claims 1 to 6 onto the primer coating, and

(iv) heating the coating of the coating composition for curing.

35 [Claim 13] A method for providing a plastic substrate with a weather and abrasion-resistant coating, comprising the steps of:

(i) applying an organic solvent solution of the primer coating composition of any one of claims 8 to 11 onto a plastic substrate,

5 (ii) evaporating the organic solvent and curing the primer coating,

(iii) applying a colloidal silica-laden organopolysiloxane composition onto the primer coat, said organopolysiloxane composition comprising a hydrolyzate or co-hydrolyzate of an organoxysilane of the following general
10 formula (D):



wherein R^{10} is selected from the class consisting of a alkyl
15 group, aryl group, halogenated alkyl group, halogenated aryl group and alkenyl group of 1 to 10 carbon atoms, and an organic group having an epoxy, (meth)acryloxy, mercapto, amino or cyano group, R^8 is hydrogen or a monovalent organic group of 1 to 10 carbon atoms, and t is equal to 0, 1 or 2,
20 and colloidal silica, and

(iv) heating the coating of the organopolysiloxane composition for curing.

[Claim 14] The method of claim 12 or 13 wherein the plastic substrate is comprised of a polycarbonate resin.

25 [Claim 15] The method of claim 14 wherein the polycarbonate resin is transparent.

[Claim 16] An article having a coating with improved weather resistance and abrasion resistance, the coating including the primer coat layer and the overcoat layer
30 formed by claim 12 or 13.

[DETAILED EXPLANATION OF THE INVENTION]

[0001]

[Technical Field of the Invention]

This invention relates to coating compositions for
35 forming mar and weather-resistant protective coatings on plastic substrates, typically polycarbonate resin substrates currently often used as structural members instead of glass in building and vehicle windows, instrument cover, and the

like, a coating method using the coating compositions, and coated articles having coatings thereof.

[0002]

[Prior Art and Problem to be Solved by the Invention]

5 As glazing substitutes, shatterproof or highly shatter resistant transparent materials have been widely utilized for these decades. For example, plastic substrates, especially polycarbonate resins have superior transparency, impact resistance and heat resistance and are currently used
10 as structural members instead of glass in a variety of applications including building and vehicle windows and instrument covers.

[0003]

15 The polycarbonate resins, however, are inferior to glass in surface properties such as mar resistance and weather resistance. It is desired to improve the surface properties of polycarbonate resin parts. Nowadays, polycarbonate resin parts for use as vehicle windows and acoustic barrier walls along highways are required to
20 withstand more than 10 years of weathering.

[0004]

Known means for improving the weather resistance of polycarbonate resin parts include the lamination of a weather resistant acrylic resin film on the surface of a
25 polycarbonate resin substrate and the formation of a ultraviolet absorber-containing resin layer on the resin surface, for example, by co-extrusion.

[0005]

30 For improving the mar resistance of polycarbonate resin parts, it is known to coat thermosetting resins such as polyorganosiloxanes and melamine resins and to coat photo-curable resins such as polyfunctional acrylic resins.

[0006]

35 As to the manufacture of transparent articles having both weather resistance and mar resistance, JP-A 56-92059 and JP-A 1-149878 disclose ultraviolet-absorbing transparent substrates having a primer layer loaded with a large amount

of UV-absorber added and a protective coating of colloidal silica-containing polysiloxane paint overlying the primer layer.

[0007]

5 However, several problems arise with this approach. The addition of a large amount of UV-absorber can adversely affect the adhesion to the substrate. During heat curing step, the UV-absorber can volatilize off. On outdoor use over a long period of time, the UV-absorber will gradually
10 bleed out, causing whitening. From the mar resistance standpoint, it is impossible to add a large amount of UV-absorber to the protective coating of colloidal silica-containing polysiloxane.

[0008]

15 From these considerations, it was also attempted to fix a UV-absorber by silyl modification. For example, JP-A 57-21476 discloses alkylcarbamylation products of alkoxy-silyl or alkanoyl-silyl. Also USP 4,316,033 and 4,349,602 disclose silyl addition products obtained by
20 reacting benzotriazole compounds with halogenated allyl compounds in the presence of bases.

[0009]

 These methods, however, involve complex steps and are uneconomical. Further, in JP-A 9-286912, the reaction
25 product of a (meth)acrylic acid derivative of benzotriazole with an amino group-containing silane compound is added to a room temperature curable composition for the purpose of imparting weather resistance. In Japanese Patent Nos. 2,885,669, 2,885,671, and 2,885,672, a silyl-modified
30 UV-absorber in the form of a reaction product resulting from addition reaction between a benzotriazole containing a polymerizable vinyl group and a silane or silicone compound containing a Si-H group is used in cosmetic compositions as the sunscreen agent.

35 [0010]

 These silyl-modified UV-absorbers are advantageous in that because of the inclusion of alkoxy-silyl groups which

undergo condensation reaction during the heat curing step, the absorbers are fixed within the coating during the heat curing step so that the absorbers might not bleed out. Heretofore, coating compositions having such silyl-modified UV-absorbers added thereto and capable of forming mar and weather-resistant coatings have not been proposed.

[0011]

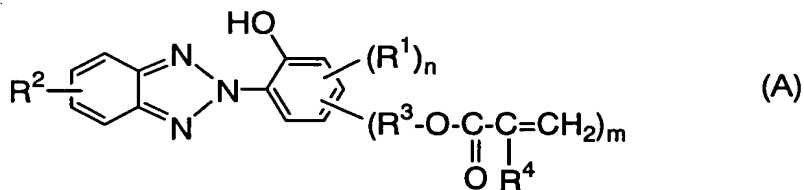
Accordingly, an object of the invention is to provide a coating composition and method for forming a protective coating having improved mar and weather resistance by using a silyl-modified ultraviolet absorber, and to provide a coated article.

[0012]

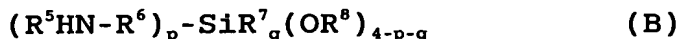
[Means for Solving the Problem and Embodiment of the Invention]

The present inventors have earnestly studied in order to attain the above object. As a result, it has been found that the reaction product of a benzotriazole compound having a polymerizable vinyl group and a hydroxyl group with a silane compound and/or a (partial) hydrolyzate thereof and preferably the reaction product of a compound of the general formula (A) with an amino group-containing organoxysilane of the general formula (B) and/or a (partial) hydrolyzate thereof becomes an effective component in a coating composition.

[0013]



Herein R¹ and R² each are hydrogen, a halogen atom or alkyl group of 1 to 10 carbon atoms, R³ is a substituted or unsubstituted divalent hydrocarbon group of 1 to 18 carbon atoms, R⁴ is hydrogen or an alkyl group of 1 to 4 carbon atoms, n is an integer of 0 to 2, and m is an integer of 1 to 3.



Herein R^5 is hydrogen or an alkyl group of 1 to 15 carbon atoms, R^6 is a divalent hydrocarbon group of 1 to 15 carbon atoms or an amino group-containing divalent hydrocarbon group of 1 to 15 carbon atoms, R^7 is an alkyl group or aryl group of 1 to 10 carbon atoms, R^8 is hydrogen or a monovalent organic group of 1 to 10 carbon atoms, p is equal to 1 or 2, q is equal to 0 or 1, and $p+q$ is equal to 1 or 2.

[0014]

Studying a coating composition for improving the mar and weather resistance of molded parts of thermoplastic resins such as polycarbonate, the inventors have discovered that a silyl-modified benzotriazole compound is so compatible with other components in the coating composition due to the effect of silyl groups that the silyl-modified benzotriazole compound may be added in larger amounts, as compared with unmodified benzotriazole compounds. The silyl-modified benzotriazole compound, even when added in large amounts, does not exacerbate the adhesion to the substrate or to the primer layer.

[0015]

It has been found that outstanding weather resistance is established because the UV-absorber can be loaded in large amounts and does not bleed out due to the fixation effect of silyl groups. Further, the component ratios and amounts of the coating composition are detailedly investigated, and thus the invention has been completed.

[0016]

Accordingly, the present invention provides the following coating composition, coating method, and coated article.

[I] A coating composition comprising the reaction product of a benzotriazole compound having a polymerizable vinyl group and a hydroxyl group with a silane compound and/or a (partial) hydrolyzate thereof.

[II] The coating composition wherein the above reaction product and/or (partial) hydrolyzate is the reaction product obtained by effecting addition reaction between the compound of the above general formula (A) and the amino

5 group-containing organoxysilane of the above general formula (B) and/or a (partial) hydrolyzate thereof.

[III] The coating composition comprising

(1) 0.1 to 100 parts by weight of the reaction product of [I] or [II] and/or the (partial) hydrolyzate thereof, and

10 (2) 100 parts by weight of a silane compound of the general formula (C):



15 wherein R^9 is an alkyl group, aryl group, halogenated alkyl group, halogenated aryl group or alkenyl group of 1 to 10 carbon atoms, or an organic group having an epoxy, (meth)acryloxy, mercapto, amino or cyano group, R^7 is an alkyl group or aryl group of 1 to 10 carbon atoms, R^8 is
20 hydrogen or a monovalent organic group of 1 to 10 carbon atoms, r and s each are equal to 0, 1 or 2, and $r+s$ is equal to 0, 1 or 2, and/or a hydrolyzate thereof.

[IV] The coating composition comprising a co-hydrolyzate obtained by subjecting to co-hydrolysis (1) 0.1 to 100 parts
25 by weight of the reaction product of [I] or [II] and/or the (partial) hydrolyzate thereof, and (2) 100 parts by weight of the silane compound of the general formula (C) and/or hydrolyzate thereof.

[V] The coating composition further comprising (3) a
30 microparticulate inorganic oxide containing at least one atom selected from titanium, cerium and zinc and capable of absorbing light having a wavelength of up to 400 nm.

[VI] The coating composition further comprising (4) colloidal silica.

35 [VII] An article having a protective coating with improved weather resistance and abrasion resistance, the coating being formed from the above coating composition.

[VIII] A primer coating composition comprising

(1) 0.1 to 50 parts by weight of the reaction product of [I] or [II] and/or (partial) hydrolyzate thereof, and

5 (5) 100 parts by weight of an organic copolymer of an acrylic and/or vinyl monomer containing an alkoxysilyl group with another monomer copolymerizable therewith, the acrylic and/or vinyl monomer containing an alkoxysilyl group accounting for 0.1 to 50% by weight of the copolymer.

[IX] The primer coating composition further comprising
10 0.1 to 50 parts by weight of a compound containing a nitrogen atom and an alkoxysilyl group in one molecule.

[X] The primer coating composition wherein the compound containing a nitrogen atom and an alkoxysilyl group in one molecule is a compound containing at least one nitrogen atom
15 and at least two alkoxysilyl groups in one molecule.

[XI] The primer coating composition further comprising 0.1 to 10 parts by weight of a photo-stabilizer having at least one cyclic hindered amine structure in a molecule.

[XII] A method for providing a plastic substrate with a weather resistant, abrasion resistant coating, comprising
20 the steps of:

(i) applying an organic solvent solution of the primer coating composition onto a plastic substrate,

25 (ii) evaporating the organic solvent and curing the primer coating,

(iii) applying the coating composition onto the primer coating, and

(iv) heating the coating of the coating composition for curing.

30 [XIII] A method for providing a plastic substrate with a weather and abrasion-resistant coating, comprising the steps of:

(i) applying an organic solvent solution of the primer coating composition onto a plastic substrate,

35 (ii) evaporating the organic solvent and curing the primer coating,

(iii) applying a colloidal silica-laden organopolysiloxane composition onto the primer coat, said organopolysiloxane composition comprising a hydrolyzate or co-hydrolyzate of an organoxysilane of the following general formula (D):



wherein R^{10} is selected from the class consisting of a alkyl group, aryl group, halogenated alkyl group, halogenated aryl group and alkenyl group of 1 to 10 carbon atoms, and an organic group having an epoxy, (meth)acryloxy, mercapto, amino or cyano group, R^8 is hydrogen or a monovalent organic group of 1 to 10 carbon atoms, and t is equal to 0, 1 or 2, and colloidal silica, and

(iv) heating the coating of the organopolysiloxane composition for curing.

[XIV] An article having a coating with improved weather resistance and abrasion resistance, the coating including the primer coat layer and the overcoat layer formed by the above methods.

[0017]

The following is the detailed description of the invention.

The inventive coating composition contains as an essential component the reaction product of a benzotriazole compound having a polymerizable vinyl group and a hydroxyl group with a silane compound and/or a (partial) hydrolyzate thereof. The reaction product results from addition reaction of the silane with the polymerizable vinyl group on the benzotriazole compound.

[0018]

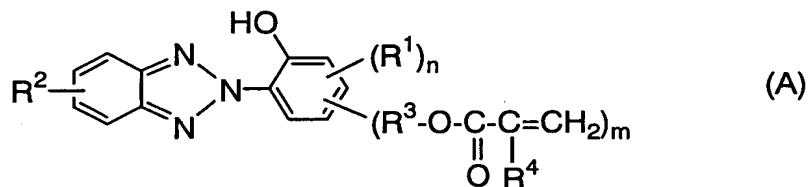
Any desired benzotriazole compound may be used herein as long as it has a polymerizable vinyl group and a hydroxyl group. In particular, compounds of the general formula (A) are preferred. On the other hand, any desired silane may be used as long as it has a functional group capable of reaction with the polymerizable vinyl group on the

benzotriazole compound. Amino group-containing silanes and thiol group-containing silanes are preferred, and in particular, amino group-containing organoxysilanes of the general formula (B) are preferred.

5 [0019]

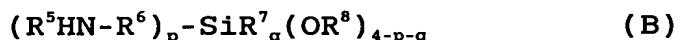
Accordingly, in the present invention, the coating composition is preferably defined as comprising the reaction product of a benzotriazole compound of the general formula (A) with an amino group-containing silane of the general formula (B) and/or (partial) hydrolyzate. Specifically, the reaction product results from Michael addition reaction between polymerizable vinyl groups on the benzotriazole UV-absorber (A) and amino groups on the amino group-containing organoalkoxysilane (B).

15 [0020]



Herein R¹ and R² each are hydrogen, a halogen atom or alkyl group of 1 to 10 carbon atoms, R³ is a substituted or unsubstituted divalent hydrocarbon group of 1 to 18 carbon atoms, R⁴ is hydrogen or an alkyl group of 1 to 4 carbon atoms, n is an integer of 0 to 2, and m is an integer of 1 to 3.

[0021]



Herein R⁵ is hydrogen or an alkyl group of 1 to 15 carbon atoms, R⁶ is a divalent hydrocarbon group of 1 to 15 carbon atoms or an amino group-containing divalent hydrocarbon group of 1 to 15 carbon atoms, R⁷ is an alkyl group or aryl group of 1 to 10 carbon atoms, R⁸ is hydrogen or a monovalent organic group of 1 to 10 carbon atoms, p is equal to 1 or 2, q is equal to 0 or 1, and p+q is equal to 1 or 2.

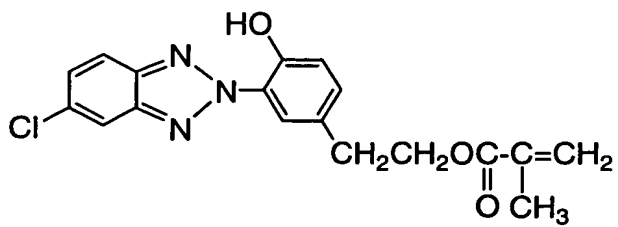
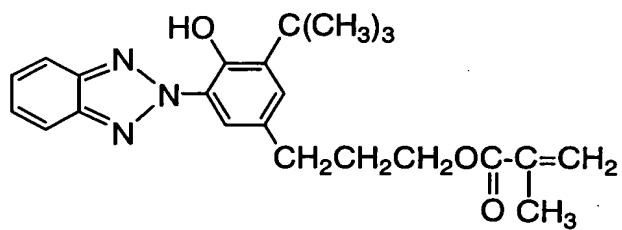
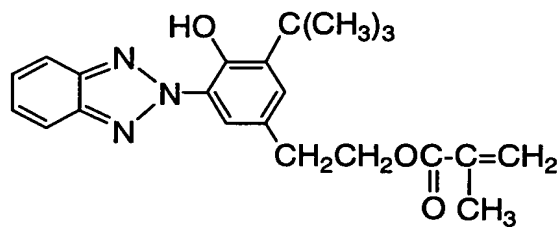
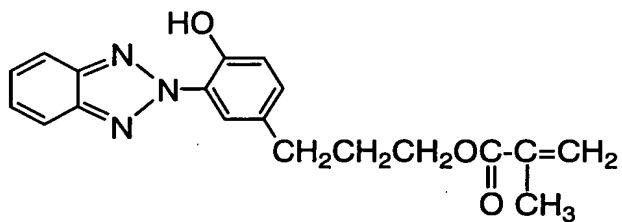
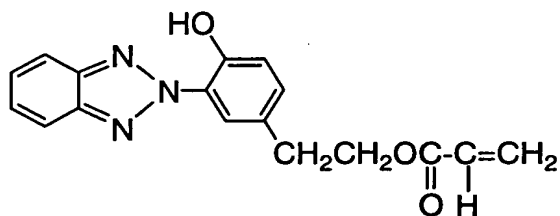
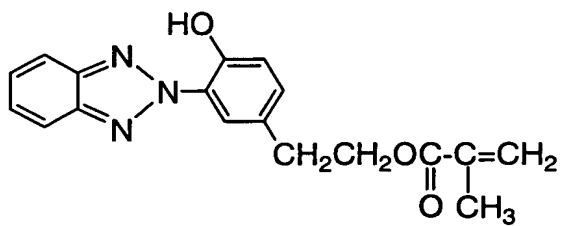
[0022]

In formula (A), R^1 and R^2 stand for hydrogen, halogen atoms such as chlorine, bromine and fluorine, and alkyl groups of 1 to 10 carbon atoms, preferably 1 to 4 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, hexyl, octyl and decyl. R^3 stands for divalent hydrocarbon groups of 1 to 18 carbon atoms, preferably 1 to 4 carbon atoms, for example, alkylene groups such as methylene, ethylene, trimethylene, propylene, tetramethylene, 1,1-dimethyltetramethylene, butylene, octylene and decylene, and substituted alkylene groups in which some hydrogen atoms are replaced by halogen atoms, hydroxyl groups or the like. R^4 is hydrogen or an alkyl group of 1 to 4 carbon atoms, such as methyl. The letter n is equal to 0, 1 or 2, and m is equal to 1, 2 or 3, and $n+m$ is up to 4.

[0023]

Illustrative, non-limiting, examples of the compound (A) are given below.

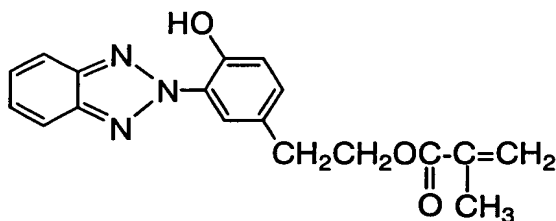
[0024]



[0025]

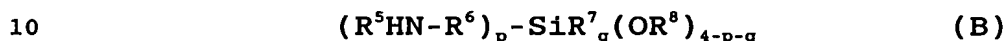
Of these, 2-(2'-hydroxy-5'-methacryloxyethylphenyl)-2H-benzotriazole of the following structure is especially preferred.

5 [0026]



[0027]

On the other hand, the amino group-containing organoxysilane is represented by of the general formula (B).



[0028]

Herein R^7 stands for alkyl groups or aryl groups of 1 to 10 carbon atoms, for example, methyl, ethyl, propyl, hexyl, decyl and phenyl. R^8 stands for hydrogen or monovalent organic groups of 1 to 10 carbon atoms, examples of which include alkyl, alkenyl, alkoxyalkyl, and acyl groups, with the alkyl and acyl groups being preferred. Illustrative examples are methyl, ethyl, propyl, isopropyl, butyl, hexyl, phenyl, isopropenyl, methoxyethyl and acetyl groups. The letter p is equal to 1 or 2, q is equal to 0 or 1, and $p+q$ is equal to 1 or 2.

[0029]

Since the amino group-containing organoxysilane must have a function of securing to the substrate, it is undesirable to use those compounds in which the number of hydrolyzable groups (OR^8) is 0 or 1, that is, $(p+q)$ is equal to 3 or 4.

[0030]

30 R^5 stands for hydrogen or alkyl groups of 1 to 15 carbon atoms, especially 1 to 4 carbon atoms. R^6 stands for organic groups, that is, divalent hydrocarbon groups of 1 to

15 carbon atoms, especially 1 to 6 carbon atoms, typically
alkylene groups, or amino group-containing divalent
hydrocarbon groups of 1 to 15 carbon atoms, especially 1 to
6 carbon atoms, typically alkylene groups which are
5 separated by an imino or alkylimino group such as NH, N(CH₃)
or N(C₂H₅). Examples of the alkyl and alkylene groups are as
exemplified above. Examples of R⁵-HN-R⁶- are given below.

H₂NCH₂-

H(CH₃)NCH₂-

10 H₂NCH₂CH₂-

H(CH₃)NCH₂CH₂-

H₂NCH₂CH₂CH₂-

H(CH₃)NCH₂CH₂CH₂-

(CH₃)₂NCH₂CH₂CH₂-

15 H₂NCH₂CH₂NHCH₂CH₂CH₂-

H(CH₃)NCH₂CH₂NHCH₂CH₂CH₂-

(CH₃)₂NCH₂CH₂NHCH₂CH₂CH₂-

H₂NCH₂CH₂NHCH₂CH₂NHCH₂CH₂CH₂-

H(CH₃)NCH₂CH₂NHCH₂CH₂NHCH₂CH₂CH₂-

20 Of these,

H₂NCH₂CH₂CH₂- and

H₂NCH₂CH₂NHCH₂CH₂CH₂- are preferred.

[0031]

Illustrative examples of the amino group-containing
25 organoxysilane of formula (B) include
3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane,
3-aminopropylmethyldimethoxysilane,
3-aminopropylmethyldiethoxysilane,
N-(2-aminoethyl)-3-aminopropyltrimethoxysilane,
30 N-(2-aminoethyl)-3-aminopropyltriethoxysilane,
N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane,
N-(2-aminoethyl)-3-aminopropylmethyldiethoxysilane,
3-(trimethoxysilylpropyl)aminopropyltrimethoxysilane,
3-(triethoxysilylpropyl)aminopropyltriethoxysilane,
35 2-(trimethoxysilylpropyl)aminoethyl-3-aminopropyltrimethoxy-
silane, and

2-(triethoxysilylpropyl)aminoethyl-3-aminopropyltriethoxysilane. Preferred from the standpoints of solubility in the coating composition and reactivity with polymerizable vinyl groups are 3-aminopropyltrimethoxysilane,

- 5 3-aminopropyltriethoxysilane,
3-aminopropylmethyldimethoxysilane,
3-aminopropylmethyldiethoxysilane,
N-(2-aminoethyl)-3-aminopropyltrimethoxysilane,
N-(2-aminoethyl)-3-aminopropyltriethoxysilane,
10 N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, and
N-(2-aminoethyl)-3-aminopropylmethyldiethoxysilane.

[0032]

In the practice of the invention, compounds (A) and compounds (B) each may be used singly or in admixture of two
15 or more.

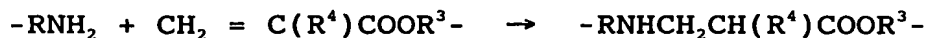
[0033]

The amounts of compounds (A) and (B) are not critical although it is preferred to use 0.5 to 3 mol, and more preferably 1 to 2 mol of compound (A) per mol of compound
20 (B). With less than 0.5 mol of compound (A) used, the absolute amount of component (A) participating in UV absorption becomes small. With more than 3 mol of compound (A) used, the reaction product may become less soluble in the coating composition and less effective for securing to
25 the substrate, leading to poor weather resistance.

[0034]

When compounds (A) and (B) are mixed and heated, addition reaction readily takes place between them as shown by the following scheme.

30



[0035]

This reaction is preferably carried out by heating
35 compounds (A) and (B) at a temperature of 20 to 180°C for 1 to 20 hours. The reaction may be effected without a solvent or in a solvent in which both compounds (A) and (B) are soluble. For easy control of reaction and ease of handling,

a polar solvent is preferably used. Exemplary solvents are tetrahydrofuran, dioxane, and dimethylformamide.

[0036]

In the practice of the invention, a partial or
5 complete hydrolyzate of the reaction product may be used as well. The hydrolyzate of the reaction product can be prepared by adding water to a lower alcohol solution of the silane compound in the presence of an acid catalyst, thereby effecting hydrolysis. Exemplary lower alcohols are
10 methanol, ethanol, isopropanol and butanol. Solvents compatible with these alcohols include ketones such as acetone and acetylacetone, esters such as ethyl acetate and isobutyl acetate, and ethers such as propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, and
15 diisopropyl ether.

[0037]

To the coating composition of the invention comprising the reaction product and/or (partial) hydrolyzate (1) as the essential component, component (2) may be added as an
20 optional component.

[0038]

The second component [Component (2)] is a silane compound of the general formula (C) and/or a hydrolyzate thereof.

25



[0039]

Herein R^9 is an alkyl group, aryl group, halogenated
30 alkyl group, halogenated aryl group or alkenyl group of 1 to 10 carbon atoms, or an organic group having an epoxy, (meth)acryloxy, mercapto, amino or cyano group. Examples include alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, hexyl, decyl and cyclohexyl; aryl groups
35 such as phenyl and phenethyl; halogenated alkyl groups such as 3-chloropropyl, 3,3,3-trifluoropropyl, and 3,3,4,4,5,5,6,6,6-nonafluorohexyl; halogenated aryl groups such as p-chlorophenyl; alkenyl groups such as vinyl, allyl,

9-decenyl and p-vinylbenzyl; epoxy group-containing organic groups such as 3-glycidoxypropyl,

β -(3,4-epoxycyclohexyl)ethyl and 9,10-epoxydecyl;

(meth)acryloxy group-containing organic groups such as

5 γ -methacryloxypropyl and γ -acryloxy; mercapto group-containing organic groups such as γ -mercaptopropyl and p-mercaptomethylphenylethyl; amino group-containing organic groups such as γ -aminopropyl and (β -aminoethyl)- γ -aminopropyl; and cyano group-containing organic groups such as

10 β -cyanoethyl. R^7 and R^8 are as defined and exemplified in formula (B). The letters r and s each are equal to 0, 1 or 2, and r+s is equal to 0, 1 or 2. The silane compound used herein functions as a binder having a bonding ability.

[0040]

15 Illustrative, non-limiting, examples of the silane compounds that satisfy the above conditions include trialkoxy or triacyloxysilanes such as methyltrimethoxysilane, methyltriethoxysilane, methyltris(2-methoxyethoxy)silane, methyltriacetoxysilane, 20 methyltripropoxysilane, methyltriisopropenoxysilane, methyltributoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane, vinyltriacetoxysilane, vinyltris(2-methoxyethoxy)silane, 25 vinyltriisopropenoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, phenyltriacetoxysilane, γ -chloropropyltrimethoxysilane, γ -chloropropyltriethoxysilane, γ -chloropropyltripropoxysilane, 30 3,3,3-trifluoropropyltrimethoxysilane, γ -glycidoxypropyltrimethoxysilane, γ -glycidoxypropylmethyldimethoxysilane, γ -glycidoxypropyltriethoxysilane, γ -glycidoxypropylmethyldiethoxysilane,

- β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane,
 β -(3,4-epoxycyclohexyl)ethylmethyldimethoxysilane,
 β -(3,4-epoxycyclohexyl)ethyltriethoxysilane,
 β -(3,4-epoxycyclohexyl)ethylmethyldiethoxysilane,
5 γ -methacryloxypropyltrimethoxysilane,
 γ -acryloxypropyltrimethoxysilane,
 γ -aminopropyltrimethoxysilane, γ -aminopropyltriethoxysilane,
 γ -mercaptopropyltrimethoxysilane,
 γ -mercaptopropyltriethoxysilane,
10 N-(β -aminoethyl)- γ -aminopropyltrimethoxysilane, and
 β -cyanoethyltrimethoxysilane;
dialkoxysilanes or diacyloxysilanes such as
dimethyldimethoxysilane, dimethyldiethoxysilane,
dimethyldi(2-methoxyethoxy)silane, dimethyldiacetoxysilane,
15 dimethyldipropoxysilane, dimethyldiisopropenoxysilane,
dimethyldibutoxysilane, vinylmethyldimethoxysilane,
vinylmethyldiethoxysilane, vinylmethyldiacetoxysilane,
vinylmethyldi(2-methoxyethoxy)silane,
vinylmethyldiisopropenoxysilane,
20 phenylmethyldimethoxysilane, phenylmethyldiethoxysilane,
phenylmethyldiacetoxysilane, γ -propylmethyldimethoxysilane,
 γ -propylmethyldiethoxysilane, γ -propylmethyldipropoxysilane,
3,3,3-trifluoropropylmethyldimethoxysilane,
 γ -methacryloxypropylmethyldimethoxysilane,
25 γ -acryloxypropylmethyldimethoxysilane,
 γ -aminopropylmethyldimethoxysilane,
 γ -aminopropylmethyldiethoxysilane,
 γ -mercaptopropylmethyldimethoxysilane,
 γ -mercaptopropylmethyldiethoxysilane,
30 N-(β -aminoethyl)- γ -aminopropylmethyldimethoxysilane, and
 β -cyanoethylmethyldimethoxysilane; and

tetraalkoxysilanes such as methyl silicate, ethyl silicate, n-propyl silicate, n-butyl silicate, sec-butyl silicate, and t-butyl silicate.

[0041]

5 Partial or complete hydrolyzates of these silane compounds are also useful. These silane compounds and/or hydrolyzates thereof may be used alone or in admixture of two or more.

[0042]

10 The (partial) hydrolyzates of the above silane compounds are obtained, for example, by adding water to a lower alcohol solution of the silane compound in the presence of an acid catalyst and effecting hydrolysis. Exemplary lower alcohols are methanol, ethanol, isopropanol
15 and butanol. Solvents compatible with these alcohols include ketones such as acetone and acetylacetone, esters such as ethyl acetate and isobutyl acetate, and ethers such as propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, and diisopropyl ether.

20 [0043]

 In the coating composition of the invention, preferably 0.1 to 100 parts, and more preferably 1 to 50 parts by weight of the reaction product and/or its hydrolyzate as component (1) is blended with 100 parts by
25 weight as solids of the silane compound and/or its (partial) hydrolyzate as component (2). Blending of more than 100 parts of component (1) is uneconomical whereas less than 0.1 part of component (1) fails to provide desired weather resistance.

30 [0044]

 In one preferred embodiment of the invention, the coating composition contains a co-hydrolyzate resulting from co-hydrolysis of the reaction product and/or its (partial) hydrolyzate (1) and the silane compound and/or its (partial)
35 hydrolyzate (2). This means that the reaction product and/or its (partial) hydrolyzate (1) is previously incorporated into the hydrolyzate of the silane compound

(2). Also in this embodiment, co-hydrolysis is effected by adding water to a lower alcohol solution of the reaction product and/or its (partial) hydrolyzate (1) and the silane compound and/or its (partial) hydrolyzate (2) in the presence of an acid catalyst. Exemplary lower alcohols are methanol, ethanol, isopropanol and butanol.

[0045]

In this embodiment, 0.1 to 100 parts, especially 1 to 50 parts by weight of the reaction product and/or its (partial) hydrolyzate as component (1) is preferably mixed with 100 parts by weight of the silane compound and/or its (partial) hydrolyzate as component (2). More than 100 parts of component (1) is uneconomical and causes gelation during reaction leading to non-uniformity whereas less than 0.1 part of component (1) fails to provide desired weather resistance.

[0046]

In the coating composition of the invention, a microparticulate inorganic oxide may be blended as an optional component (3). This component is also designated an inorganic UV-absorber since it is a microparticulate inorganic oxide capable of absorbing detrimental light rays with a wavelength of up to 400 nm which can cause decomposition and degradation of organic compounds. Since oxides of titanium, cerium and zinc have an ability to absorb light rays of up to 400 nm in wavelength, the microparticulate inorganic oxide must contain at least one of titanium, cerium and zinc. If necessary, a metal oxide other than the above-described ones is added to the inorganic oxide particles in any desired manner for the purpose of stabilizing the particles or improving weather resistance, and as long as the light absorbing ability is not impaired. The manner of adding the other metal oxide includes simple addition, mechanical adsorption of the other metal oxide to the periphery of inorganic oxide particles, coating of inorganic oxide particles on their surface with a thin film of the other metal oxide, formation of mixed

crystals by the sol-gel method, and doping of inorganic oxide particles with the other metal oxide in crystal form. Examples of the other metal include Si (silica), Al (alumina), Sn (tin oxide), Zr (zirconia), Sb (antimony oxide), Fe (iron oxide), and rare earth metals (rare earth metal oxides) though not limited thereto. Of these, oxides of Si, Al, Sn and Zr are preferred. The inorganic oxide particles should preferably have a particle size of 1 to 300 μ , more preferably 1 to 200 μ . Particles with a size of greater than 300 μ may adversely affect light transmission. Particles with a size of less than 1 μ are inadequate since they are unstable and difficult to prepare. The inorganic oxide particles may be used in the form of powder, water dispersion or organic solvent dispersion.

15 [0047]

In the coating composition, preferably 0.1 to 100 parts, more preferably 1 to 80 parts by weight of the inorganic oxide particles of the third component is blended with 100 parts by weight as solids of the silane compound and/or its (partial) hydrolyzate (2). Less than 0.1 part is ineffective for further improving weather resistance and achieving the combined effect with component (1). Blending of more than 100 parts may adversely affect film strength and film transparency and is uneconomical.

25 [0048]

Preferably 0.1 to 100 parts, more preferably 2 to 20 parts by weight of the microparticulate inorganic oxide of component (3) is blended per 100 parts by weight as solids of the co-hydrolyzate of the silane compound and/or its (partial) hydrolyzate (2) and the reaction product and/or its (partial) hydrolyzate (1). Less than 0.1 part of component (3) is ineffective for further improving weather resistance and achieving the combined effect with component (1). Blending of more than 100 parts of component (3) may adversely affect film strength and film transparency.

[0049]

In the inventive coating composition, colloidal silica is preferably blended as an optional fourth component. Colloidal silica is blended in an amount of 1 to 200 parts, especially 10 to 150 parts by weight of per 100 parts by weight of component (2). One exemplary blending procedure is by mixing 20 to 90 parts by weight of the silane compound and/or its (partial) hydrolyzate (2) with 10 to 80 parts by weight as solids of a colloidal silica containing silica fines having a particle size of 1 to 100 nm to a total amount of 100 parts by weight. The mixture is diluted with alcohol, water or water-miscible solvent to a nonvolatile concentration of 15 to 20% by weight. The dilution is ripened at room temperature for 3 to 5 days or at 40 to 60°C for 10 to 15 hours. The term "colloidal silica" is a dispersion of silica fines in water or an alcohol such as methanol, ethanol, isobutanol or diacetone alcohol.

[0050]

Also, upon the above-described hydrolysis, the colloidal silica may be added along with the acid catalyst. To the colloidal silica-laden protective coating composition, a buffer solution and a curing catalyst are preferably added so as to provide adequate abrasion resistance. Examples of the curing catalyst include dimethylamine, acetic ethanol amine, formic dimethylaniline, benzoic acid, tetraethylammonium salts, sodium acetate, sodium propionate, sodium formate, and trimethylammonium benzoyl acetate. An appropriate amount of the curing catalyst added is 0.02 to 0.4 part by weight per 100 parts by weight as solids of the colloidal silica-laden protective coating composition.

[0051]

From the standpoint of insuring stability, the coating composition is preferably adjusted to pH 2 to 7, at which silanol groups remain stable, and especially pH 3 to 6. The buffer used for pH adjustment may be a combination of acidic and basic compounds, for example, a combination of acetic

acid and sodium acetate and a combination of disodium hydrogen phosphate and citric acid.

[0052]

In the coating composition, well-known additives
5 commonly used in conventional coating compositions, such as leveling agents, are blended if necessary.

[0053]

The coating composition is useful in protecting surfaces of various articles, especially plastic articles.
10 Specifically the coating composition is applied to an article substrate to form a protective coating thereon. The plastic article substrates to which the composition is applicable include those of polycarbonate, polystyrene, modified acrylic resins, urethane resins, thiourethane
15 resins, polycondensates of halogenated bisphenol A and ethylene glycol, acrylic urethane resins, halogenated aryl group-containing acrylic resins, and sulfur-containing resins. The benefits become more outstanding when the coating composition is applied to transparent plastic
20 substrates, and especially polycarbonate resins.

[0054]

In order to enhance the adhesion to the substrate, especially plastic substrate, it is preferred that a primer layer intervenes between the substrate and the coating. The
25 primer used for forming the primer layer is preferably a primer coating composition comprising above component (1) as an essential component.

[0055]

The primer coating composition of the present
30 invention contains the silyl-modified benzotriazole base compound of component (1) as an essential component.

[0056]

The constituents other than component (1) are described. An organic copolymer resin becoming a
35 predominant component in the primer coating composition is preferably an organic copolymer of an alkoxysilyl

group-containing acrylic and/or vinyl monomer with another monomer copolymerizable therewith.

[0057]

Owing to the alkoxyethyl groups introduced, the primer
5 coating composition is endowed with reactivity with the protective coating layer overlying the primer layer and improved in adhesion. Crosslinking of alkoxyethyl groups together improves heat resistance and imparts durability. Additionally, the copolymer is well compatible with the
10 reaction product, i.e., ethyl-modified benzotriazole compound.

[0058]

If the content of the alkoxyethyl group-containing monomer is less than 0.1% by weight, heat resistance and
15 durability are not improved, and compatibility with the reaction product or ethyl-modified benzotriazole compound is aggravated. If the content of the alkoxyethyl group-containing monomer is more than 50% by weight, the copolymer would become too hard, losing adhesion.
20 Therefore, the content of the alkoxyethyl group-containing acrylic and/or vinyl monomer is 0.1 to 50% by weight based on the total weight combined with the other monomer.

[0059]

Examples of the alkoxyethyl group-containing acrylic
25 monomer include 3-methacryloxypropyltrimethoxysilane, 3-methacryloxypropyltriethoxysilane, 3-methacryloxypropylmethyldimethoxysilane, 3-methacryloxypropylmethyldiethoxysilane, 3-acryloxypropyltrimethoxysilane,
30 3-acryloxypropyltriethoxysilane, 3-acryloxypropylmethyldimethoxysilane, 3-acryloxypropylmethyldiethoxysilane, 3-methacryloxymethyltrimethoxysilane, 3-methacryloxymethyltriethoxysilane,
35 3-methacryloxymethylmethyldimethoxysilane, 3-methacryloxymethylmethyldiethoxysilane, 3-acryloxymethyltrimethoxysilane,

3-acryloxymethyltriethoxysilane,
3-acryloxymethylmethyldimethoxysilane, and
3-acryloxymethylmethyldiethoxysilane. Of these,
3-methacryloxypropyltrimethoxysilane and

5 3-methacryloxypropylmethyldimethoxysilane are preferred for
ease of handling, crosslinked density and reactivity.

[0060]

Examples of the alkoxysilyl group-containing vinyl
monomer include vinyltrimethoxysilane, vinyltriethoxysilane,
10 vinyltris(2-methoxyethoxy)silane,
vinylmethyldimethoxysilane, vinylmethyldiethoxysilane,
vinylmethylbis(2-methoxyethoxy)silane,
3-vinyloxypropyltrimethoxysilane,
3-vinyloxypropyltriethoxysilane,
15 3-vinyloxypropylmethyldimethoxysilane,
3-vinyloxypropylmethyldiethoxysilane,
styryltrimethoxysilane, styryltriethoxysilane,
styrylmethyldimethoxysilane, and styrylmethyldiethoxysilane.
Of these, vinyltrimethoxysilane, vinyltriethoxysilane, and
20 3-vinyloxypropyltrimethoxysilane are preferred for ease of
handling and reactivity.

[0061]

Examples of the other monomer copolymerizable with the
alkoxysilane monomer include alkyl methacrylates such as
25 methyl methacrylate, butyl methacrylate, and
2-ethylhexyl methacrylate; alkyl acrylates such as
methyl acrylate, ethyl acrylate, and butyl acrylate;
vinyl ethers such as glycidyl methacrylate, acrylamide,
acrylonitrile, vinyl acetate, ethyl vinyl ether,
30 butyl vinyl ether, and hexyl vinyl ether; styrene and
ethylene glycol dimethacrylate; and methacrylic
group-containing benzotriazoles represented by above formula
(A) serving as a UV-absorber such as
2-(2'-hydroxy-5'-methacryloxyethylphenyl)-2H-benzotriazole.
35 It is noted that compounds having a group capable of
reacting with the alkoxysilyl group, for example,
2-hydroxyethyl methacrylate are undesirable since they can

cause the primer coating composition to change with time, typically thickening or gelling.

[0062]

The organic copolymer constituting the main component
5 of the first primer coating composition according to the invention is a copolymer of the alkoxysilyl group-containing monomer with the other monomer copolymerizable therewith. The copolymer is readily obtained by adding a radical
polymerization initiator to a solution of the monomers,
10 followed by heating to effect reaction. The initiator is selected from peroxides such as dicumyl peroxide and benzoyl peroxide and azo compounds such as azobisisobutyronitrile.

Preferably the organic copolymer have a weight average molecular weight of 1,000 to 200,000.

15 [0063]

If the organic copolymer is less than 10% by weight of the primer coating composition, the composition may become thermoplastic and less resistant to heat. If the organic copolymer exceeds 80% by weight of the primer coating
20 composition, adhesion may become poor. Therefore, an appropriate amount of the organic copolymer is 10 to 80% by weight of the primer coating composition.

[0064]

The organic copolymer and the reaction product or
25 silyl-modified benzotriazole compound (1) are blended such that 0.1 to 50 parts, especially 2 to 50 parts by weight of the reaction product (1) is available per 100 parts by weight of the organic copolymer. More than 50 parts of the reaction product (1) is uneconomical whereas less than 0.1
30 part of the reaction product (1) fails to provide the desired weather resistance.

[0065]

If the primer coating composition has a too low viscosity to apply and thus forms only a thin coating, an
35 acrylic polymer may be added as a component capable of imparting flexibility without detracting from adhesion. Such useful acrylic polymers include

poly(alkyl methacrylates) and poly(alkyl acrylates) such as poly(methyl methacrylate), poly(butyl methacrylate), and poly(butyl acrylate), and copolymers thereof. These acrylic polymers are effective for imparting flexibility to the primer coating composition without detracting from adhesion. The amount of the acrylic polymer added is desirably limited to 30% by weight or less based on the entire primer coating composition since more than 30% by weight of the acrylic polymer can preclude the composition from heat curing.

10 [0066]

In the primer coating composition, a compound containing a nitrogen atom and an alkoxysilyl group in a molecule may be added for the purposes of assisting the composition in forming a satisfactory bond having water resistance, and fixing within the coating the silyl-modified benzotriazole compound in component (1), the organic copolymer and optional photo-stabilizer by crosslinking with alkoxysilyl groups therein. Preferably the compound contains at least one nitrogen atom and at least two alkoxysilyl groups in a molecule.

20 [0067]

Preferred examples of the compound used herein include an amino group-containing alkoxysilane, amino group-containing di(alkoxysilane), amide group-containing alkoxysilane, one obtained by reacting an amino group-containing alkoxysilane with an epoxy group-containing alkoxysilane and a silylating agent and amidating the reaction product, the reaction product of an amino group-containing alkoxysilane with a polyfunctional (meth)acrylic compound, the reaction product of an amino group-containing alkoxysilane with a (meth)acrylic compound, the reaction product of an amino group-containing alkoxysilane with a (meth)acrylic group-containing alkoxysilane, the reaction product of a polyamine compound with a (meth)acrylic group-containing alkoxysilane, one obtained by reacting an amino group-containing alkoxysilane with a polyfunctional isocyanate compound and amidating the

reaction product, one obtained by reacting an amino group-containing alkoxy silane with an isocyanate group-containing alkoxy silane and amidating the reaction product, and the reaction product of a thiol group-containing alkoxy silane with an isocyanate group-containing alkoxy silane. Of these, preferred is the one obtained by reacting an amino group-containing alkoxy silane with an epoxy group-containing alkoxy silane and a silylating agent and amidating the reaction product.

10 [0068]

Illustrative examples of the components used herein are described. Examples of the amino group-containing alkoxy silane include 3-aminopropyltrimethoxy silane, 3-aminopropyltriethoxy silane, 15 3-aminopropylmethyldimethoxy silane, 3-aminopropylmethyldiethoxy silane, N-(2-aminoethyl)-3-aminopropyltrimethoxy silane, N-(2-aminoethyl)-3-aminopropyltriethoxy silane, N-(2-aminoethyl)-3-aminopropylmethyldimethoxy silane, 20 N-(2-aminoethyl)-3-aminopropylmethyldiethoxy silane, 3-(trimethoxysilylpropyl)aminopropyltrimethoxy silane, 3-(triethoxysilylpropyl)aminopropyltriethoxy silane, 2-(trimethoxysilylpropyl)aminoethyl-3-aminopropyltrimethoxy silane, and 25 2-(triethoxysilylpropyl)aminoethyl-3-aminopropyltriethoxy silane.

[0069]

Examples of the amide group-containing alkoxy silane include ureidopropyltrimethoxy silane, 30 ureidopropyltriethoxy silane, ureidopropylmethyldimethoxy silane, and ureidopropylmethyldiethoxy silane.

[0070]

The process of obtaining the amide compound by 35 reacting an amino group-containing alkoxy silane with an epoxy group-containing alkoxy silane and a silylating agent and amidating the reaction product is described below. The

amino group-containing alkoxysilane is as exemplified above although N-(2-aminoethyl)-3-aminopropyltrimethoxysilane and N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane are preferred for adhesion and operation. Illustrative examples
5 of the epoxy group-containing alkoxysilane include
 γ -glycidoxypropyltrimethoxysilane,
 γ -glycidoxypropylmethyldimethoxysilane,
 γ -glycidoxypropyltriethoxysilane,
 γ -glycidoxypropylmethyldiethoxysilane,
10 β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane,
 β -(3,4-epoxycyclohexyl)ethylmethyldimethoxysilane,
 β -(3,4-epoxycyclohexyl)ethyltriethoxysilane, and
 β -(3,4-epoxycyclohexyl)ethylmethyldiethoxysilane. From the
standpoints of reactivity and ease of operation, the
15 preferred silane compounds are
 γ -glycidoxypropyltrimethoxysilane,
 γ -glycidoxypropylmethyldimethoxysilane, and
 β -(3,4-epoxycyclohexyl)ethylmethyldimethoxysilane.

[0071]

20 Examples of the silylating agent include
hexamethyldisilazane, N,N'-bis(trimethylsilyl)formamide and
N,N'-bis(trimethylsilyl)urea. When the amino
group-containing alkoxysilane reacts with an epoxy
group-containing alkoxysilane, the silylating agent serves
25 to protect the OH groups generated by the reaction for
preventing reaction between OH groups and alkoxysilyl
groups, thereby precluding a change with time of the
reaction product.

[0072]

30 Reaction of the amino group-containing alkoxysilane
with the epoxy group-containing alkoxysilane and the
silylating agent may be effected by adding dropwise the
epoxy group-containing alkoxysilane to a mixture of the
amino group-containing alkoxysilane and the silylating agent

and heating the mixture for reaction. Alternatively, the amino group-containing alkoxysilane is reacted with the epoxy group-containing alkoxysilane, and the silylating agent is added to the reaction product for further reaction.

5 [0073]

In this reaction, the amino group-containing alkoxysilane and the epoxy group-containing alkoxysilane are preferably used in such amounts that the molar ratio of epoxy groups to amino (=N-H) groups may range from 0.3/1 to 1.2/1. If the molar ratio of epoxy/amino is less than 0.3, only a less number of alkoxy groups per molecule participate in crosslinking, leading to short cure, and the entire molecule is not spread, leading to a weak surface bond. If the molar ratio of epoxy/amino is more than 1.2, amino (=N-H) groups which can be amidated during subsequent amidation step become few, exacerbating water-resistant bond.

[0074]

The reaction product is then amidated. For amidation, the reaction product may be reacted with a carboxylic acid halide, acid anhydride or acid isopropenyl ester such as acetic chloride, acetic bromide, propionic chloride, acetic anhydride, isopropenyl acetate or benzoyl chloride.

[0075]

25 In the primer coating composition, 0.5 to 20 parts by weight of the compound is preferably blended per 100 parts by weight of the organic copolymer. An excessive amount of the compound may result in a primer layer having a too high crosslinked density, a high hardness, and rather poor adhesion.

[0076]

In the primer coating composition, a photo-stabilizer having at least one cyclic hindered amine structure in a molecule may be added for improving weather resistance.

35 [0077]

The photo-stabilizer used herein should preferably be fully soluble in the solvent of the primer coating

composition, compatible with the organic copolymer, and low volatile. In the primer coating composition, 2.6 to 10 parts by weight of the photo-stabilizer is preferably blended per 100 parts by weight of the organic copolymer.

- 5 More than 10 parts of the photo-stabilizer detracts from adhesion of a coating.

[0078]

- Illustrative examples of the photo-stabilizer include
- 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidiny)pyrrolidine-
10 2,5-dione,
N-methyl-3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidiny)-
pyrrolidine-2,5-dione,
N-acetyl-3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidiny)-
pyrrolidine-2,5-dione,
15 bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate,
bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate,
tetrakis(2,2,6,6-tetramethyl-4-piperidyl)
1,2,3,4-butanetetracarboxylate,
tetrakis(1,2,2,6,6-pentamethyl-4-piperidyl) 1,2,3,4-butane-
20 tetracarboxylate,
a condensate of 1,2,3,4-butanetetracarboxylic acid with
2,2,6,6-tetramethyl-piperidinol and tridecanol,
8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro-
[4,5]decane-2,4-dione,
25 a condensate of 1,2,3,4-butanetetracarboxylic acid with
1,2,6,6-tetramethyl-4-piperidinol and
 β,β,β,β' -tetramethyl-3,9-(2,4,8,10-tetraoxaspiro[5,5]-
undecane)diethanol, and a condensate of
1,2,3,4-butanetetracarboxylic acid with
30 2,2,6,6-tetramethyl-4-piperidinol and
 β,β,β,β' -tetramethyl-3,9-(2,4,8,10-tetraoxaspiro[5,5]-
undecane)diethanol. For the purpose of fixing the
photo-stabilizer, there may be also used silyl-modified
photo-stabilizers as disclosed in JP-B 61-56187, for example,
35 2,2,6,6-tetramethylpiperidino-4-propyltrimethoxysilane,
2,2,6,6-tetramethylpiperidino-4-propylmethyldimethoxysilane,
2,2,6,6-tetramethylpiperidino-4-propyltriethoxysilane, and

2,2,6,6-tetramethylpiperidino-4-propylmethyldiethoxysilane as well as (partial) hydrolyzates thereof. These photo-stabilizers may be used in admixture of two or more.

[0079]

5 In the primer coating composition, a conventional ultraviolet absorber which has not been silyl modified may be added insofar as no detrimental effect is exerted. Such UV-absorbers are organic UV-absorbers compatible with the organic copolymer. Derivatives of compounds having a
10 hydroxybenzophenone, benzotriazole, cyanoacrylate or triazine main skeleton are especially preferred. Also acceptable are polymers such as vinyl polymers having such a UV-absorber incorporated on a side chain. Exemplary UV-absorbers are 2,4'-dihydroxybenzophenone,
15 2,2',4,4'-tetrahydroxybenzophenone,
2-hydroxy-4-methoxybenzophenone,
2-hydroxy-4-methoxybenzophenone-5-sulfonic acid,
2-hydroxy-4-n-octoxybenzophenone,
2-hydroxy-4-n-dodecyloxybenzophenone,
20 2-hydroxy-4-n-benzyloxybenzophenone,
2,2'-dihydroxy-4,4'-dimethoxybenzophenone,
2,2'-dihydroxy-4,4'-diethoxybenzophenone,
2,2'-dihydroxy-4,4'-dipropoxybenzophenone,
2,2'-dihydroxy-4,4'-dibutoxybenzophenone,
25 2,2'-dihydroxy-4-methoxy-4'-propoxybenzophenone,
2,2'-dihydroxy-4-methoxy-4'-butoxybenzophenone,
2,3,4-trihydroxybenzophenone,
2-(2-hydroxy-5-t-methylphenyl)benzotriazole,
2-(2-hydroxy-5-t-octylphenyl)benzotriazole,
30 2-(2-hydroxy-3,5-di-t-butylphenyl)benzotriazole,
ethyl-2-cyano-3,3-diphenyl acrylate,
2-ethylhexyl-2-cyano-3,3-diphenyl acrylate,
2-(2-hydroxy-4-hexyloxyphenyl)-4,6-diphenyltriazine,
4-(2-acryloxyethyl)-2-hydroxybenzophenone polymer, and
35 2-(2'-hydroxy-5'-methacryloxyethylphenyl)-2H-benzotriazole polymer. Of these, 2,2',4,4'-tetrahydroxybenzophenone is most preferred from the standpoints of compatibility with

the primer coating composition and volatility. These organic UV-absorbers may be used in admixture of two or more.

[0080]

5 On use, the primer coating composition is diluted with a solvent. Useful solvents include diacetone alcohol, propylene glycol monomethyl ether, ethylene glycol monomethyl ether, propylene glycol monoethyl ether, ethylene glycol monoethyl ether, isobutyl alcohol, isopropyl alcohol, 10 n-butyl alcohol, n-propyl alcohol, acetone, methyl ethyl ketone, methyl isobutyl ketone, acetyl acetone, ethyl acetate, butyl acetate, xylene, and toluene. The primer coating composition is generally diluted with the solvent into a solution containing 5 to 10% by weight of the organic 15 copolymer prior to use.

[0081]

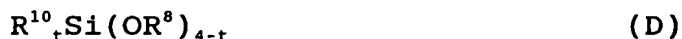
20 The primer coating composition is applied to a surface of a plastic substrate, typically a plastic film, which has been cleaned, whereupon the diluting solvent is evaporated off at room temperature or elevated temperature, leaving a dry undercoat of 1 to 10 μm , preferably 2 to 5 μm thick. The organic solvent dilution should preferably have a viscosity of 5 to 30 centistokes. A dilution with a viscosity of less than 5 centistokes would be difficult to form a thick coat 25 whereas a dilution with a viscosity of more than 30 centistokes would be difficult to handle and apply. To the composition, a fluorine or silicone surfactant may be added for leveling of the coating, and a catalytic amount of a crosslinking/curing catalyst may also be added for 30 accelerating cure.

[0082]

35 The plastic substrates such as plastic films and sheets with the cured coat or primer layer of the primer coating composition of the present invention are improved in initial adhesion, heat resistance, hot-water resistance, and weather resistance. A topcoat is formed on the primer layer with the inventive coating composition or the known

colloidal silica-containing organopolysiloxane composition. For example, the known composition comprises a hydrolyzate or co-hydrolyzate of an organoxysilane of the following general formula (D):

5



wherein R^{10} is selected from the class consisting of a alkyl group, aryl group, halogenated alkyl group, halogenated aryl group and alkenyl group of 1 to 10 carbon atoms, and an organic group having an epoxy, (meth)acryloxy, mercapto, amino or cyano group as in R^9 of formula (C), R^8 is hydrogen or a monovalent organic group of 1 to 10 carbon atoms as in R^8 of formula (B), and t is equal to 0, 1 or 2, and 5 to 70% by weight of colloidal silica having 1 to 100 m μ which is dispersed in water or alcohol such as methanol, ethanol, isobutanol and diacetone alcohol. The top coat is formed by applying and heating the composition especially to 50-140°C to cure it. The resulting plastic article has the inventive primer coating composition layer applied at its surface. The top coat of the inventive coating composition or organopolysiloxane synergistically cooperates with the primer coat of the primer coating composition to accomplish high adhesion and abrasion resistance as well as excellent weather resistance and its stability due to tight fixation of the UV-absorber in the primer coat.

[0083]

The coating composition or primer coating composition is useful in protecting surfaces of various articles, especially plastic articles. Specifically the coating composition is applied to an article substrate to form a protective coating thereon. The plastic article substrates to which the composition is applicable include those of polycarbonate, polystyrene, modified acrylic resins, urethane resins, thiourethane resins, polycondensates of halogenated bisphenol A and ethylene glycol, acrylic urethane resins, halogenated aryl group-containing acrylic

resins, and sulfur-containing resins. The benefits become more outstanding when the coating composition is applied to transparent plastic substrates, and especially polycarbonate resins.

5 [0084]

[EXAMPLE]

Synthesis Examples, Examples and Comparative Examples of the invention are given below by way of illustration and not by way of limitation. All parts and percents are by
10 weight.

<Synthesis of silyl-modified UV-absorbers>

[Synthesis Example 1]

A 0.5-liter flask equipped with a stirrer, condenser and thermometer was charged with 161.5 g (0.50 mol) of
15 2-(2'-hydroxy-5'-methacryloxyethylphenyl)-2H-benzotriazole, 89.5 g (0.50 mol) of γ -aminopropyltrimethoxysilane, and 251 g of dimethylformamide, which were stirred and heated at 80°C for dissolution. At this point, the solution was yellow and clear. The solution was heated to 120°C, at which
20 temperature reaction was effected for 5 hours, obtaining a brown clear solution. By gas chromatography analysis, the disappearance of the reactant, γ -aminopropyltrimethoxysilane was confirmed. The solid concentration was 50.1%. A dilution obtained by diluting the solution with
25 dichloromethane to a solid concentration of 0.05 g/liter was analyzed for absorbance by spectrophotometry, finding an absorbance: λ_{\max} 341.4 nm and Abs 1.75, which was substantially identical with the absorbance of the reactant, 2-(2'-hydroxy-5'-methacryloxyethylphenyl)-2H-benzotriazole
30 as analyzed at the same concentration: λ_{\max} 342.7 nm and Abs 1.85, with the light absorption waveform of the former being also substantially identical with the latter.

[0085]

[Synthesis Example 2]

35 A 0.5-liter flask equipped with a stirrer, condenser and thermometer was charged with 161.5 g (0.50 mol) of

2-(2'-hydroxy-5'-methacryloxyethylphenyl)-2H-benzotriazole,
111.0 g (0.50 mol) of N-(2-aminoethyl)-3-aminopropyl-
trimethoxysilane, and 272.5 g of dimethylformamide, which
were stirred and heated at 80°C for dissolution. At this
5 point, the solution was yellow and clear. The solution was
heated to 120°C, at which temperature reaction was effected
for 4 hours, obtaining a brown clear solution. By gas
chromatography analysis, the disappearance of the reactant,
N-(2-aminoethyl)-3-aminopropyltrimethoxysilane was
10 confirmed. The solid concentration was 49.9%. A dilution
obtained by diluting the solution with dichloromethane to a
solid concentration of 0.05 g/liter was analyzed for
absorbance by spectrophotometry, finding an absorbance: λ_{max}
339.8 nm and Abs 1.66, which was substantially identical
15 with the absorbance of the reactant, 2-(2'-hydroxy-5'-
methacryloxyethylphenyl)-2H-benzotriazole as analyzed at the
same concentration: λ_{max} 342.7 nm and Abs 1.85, with the
light absorption waveform of the former being also
substantially identical with the latter.

20 [0086]

[Synthesis Example 3]

A 1.0-liter flask equipped with a stirrer, condenser
and thermometer was charged with 323.0 g (1.0 mol) of
2-(2'-hydroxy-5'-methacryloxyethylphenyl)-2H-benzotriazole,
25 89.5 g (0.50 mol) of γ -aminopropyltrimethoxysilane, and 412.5
g of dimethylformamide, which were stirred and heated at
80°C for dissolution. At this point, the solution was
yellow and clear. The solution was heated to 120°C, at
which temperature reaction was effected for 10 hours,
30 obtaining a brown clear solution. By gas chromatography
analysis, the disappearance of the reactant,
 γ -aminopropyltrimethoxysilane was confirmed. By GPC analysis
using standard polystyrene as a reference, the disappearance
of the other reactant, 2-(2'-hydroxy-5'-methacryloxyethyl-
35 phenyl)-2H-benzotriazole was also confirmed. The solid
concentration was 51.0%. A dilution obtained by diluting

the solution with dichloromethane to a solid concentration of 0.05 g/liter was analyzed for absorbance by spectrophotometry, finding an absorbance: λ_{max} 341.4 nm and Abs 2.22, which was substantially identical with the absorbance of the reactant, 2-(2'-hydroxy-5'-methacryloxyethylphenyl)-2H-benzotriazole as analyzed at the same concentration: λ_{max} 342.7 nm and Abs 1.85, with the light absorption waveform of the former being also substantially identical with the latter.

[0087]

[Synthesis Example 4]

A 1.0-liter flask equipped with a stirrer, condenser and thermometer was charged with 323.0 g (1.0 mol) of 2-(2'-hydroxy-5'-methacryloxyethylphenyl)-2H-benzotriazole, 111.0 g (0.50 mol) of N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, and 434.0 g of dimethylformamide, which were stirred and heated at 80°C for dissolution. At this point, the solution was yellow and clear. The solution was heated to 120°C, at which temperature reaction was effected for 10 hours, obtaining a brown clear solution. By gas chromatography analysis, the disappearance of the reactant, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane was confirmed. By GPC analysis using standard polystyrene as a reference, the disappearance of the other reactant, 2-(2'-hydroxy-5'-methacryloxyethylphenyl)-2H-benzotriazole was also confirmed. The solid concentration was 50.3%. A dilution obtained by diluting the solution with dichloromethane to a solid concentration of 0.05 g/liter was analyzed for absorbance by spectrophotometry, finding an absorbance: λ_{max} 341.5 nm and Abs 2.22, which was substantially identical with the absorbance of the reactant, 2-(2'-hydroxy-5'-methacryloxyethylphenyl)-2H-benzotriazole as analyzed at the same concentration: λ_{max} 342.7 nm and Abs 1.85, with the light absorption waveform of the former being also substantially identical with the latter.

[0088]

<Synthesis of alkoxysilyl-containing organic copolymers>

[Synthesis Example 5]

A 0.5-liter flask equipped with a stirrer, condenser
5 and thermometer was charged with 20 g of
 γ -methacryloxypropyltrimethoxysilane, 60 g of methyl
methacrylate, 5 g of ethyl acrylate, 5 g of vinyl acetate,
10 g of glycidyl methacrylate, 0.2 g of ethylene glycol
dimethacrylate, 0.5 g of azobisisobutyronitrile as a
polymerization initiator, and 20 g of diacetone alcohol and
80 g of ethylene glycol monomethyl ether as solvents. The
contents were stirred for 5 hours at 80 to 90°C under a
nitrogen stream. The resulting solution containing an
organic copolymer having alkoxysilyl groups had a viscosity
15 of 43,600 centistokes, and the copolymer contained 20% of
alkoxyl groups.

[0089]

[Synthesis Example 6]

The procedure of Synthesis Example 5 was repeated
20 except that the amount of γ -methacryloxypropyltrimethoxy-
silane was changed to 10 g and the amount of methyl
methacrylate was changed to 70 g, obtaining a solution
containing an organic copolymer having alkoxysilyl groups.
The organic copolymer solution had a viscosity of 40,600
25 centistokes, and the copolymer contained 10% of alkoxyl
groups.

[0090]

[Synthesis Example 7]

The procedure of Synthesis Example 5 was repeated
30 except that 20 of γ -methacryloxypropyltrimethoxysilane was
replaced by 20 g of vinyltrimethoxysilane, obtaining a
solution containing an organic copolymer having alkoxysilyl
groups. The organic copolymer solution had a viscosity of
39,700 centistokes, and the copolymer contained 20% of
35 alkoxyl groups.

[0091]

<Synthesis of compounds containing a nitrogen atom and an alkoxysilyl group in a molecule>

[Synthesis Example 8]

5 A 2.0-liter flask equipped with a stirrer, condenser and thermometer was charged with 222 g of N-2-(aminoethyl)-3-aminopropyltrimethoxysilane and 242 g of hexamethyldisilazane as a silylating agent. The contents were heated at 120°C under a nitrogen stream. To the flask,
10 496 g of γ -glycidoxypropylmethyldiethoxysilane was added dropwise for reaction. The reaction mixture was further stirred and heated at 120°C for 5 hours. A low-boiling fraction was stripped off at 100°C under vacuum, leaving 862 g of a viscous compound having a viscosity of 1,387
15 centistokes, a refractive index of 1.4618 and a specific gravity of 1.048. Next, a 2.0-liter flask equipped with a stirrer, condenser and thermometer was charged with 862 g of the reaction product and 862 g of toluene. In a nitrogen stream, 141 g of acetic anhydride was added dropwise to the
20 flask at room temperature for reaction. The reaction mixture was further stirred and heated at 110°C for 2 hours. Methanol, 141 g, was added dropwise to the reaction mixture at 50°C, which was further stirred and heated at 50°C for 1 hour. A low-boiling fraction was stripped off at 100°C
25 under vacuum, leaving a highly viscous compound.

[0092]

 This compound was analyzed by IR absorption spectroscopy, finding no absorption peaks attributable to the OH or NH group in the region of at least 3,000 cm^{-1} , but
30 a definite peak attributable to the amide group absorption at 1,650 cm^{-1} .

[0093]

<Synthesis of colloidal silica-laden organopolysiloxane composition>

35 [Synthesis Example 9]

 A 1.0-liter flask equipped with a stirrer, condenser and thermometer was charged with 164 g of

methytriethoxysilane and 46 g of isobutanol, which were maintained below 5°C under ice cooling with stirring. To this was added 138 g of colloidal silica (containing 20% of SiO₂) below 5°C. The mixture was stirred for 2 hours under ice cooling and for a further 8 hours at 20 to 25°C. Thereafter, 45 g of diacetone alcohol and 50 g of isobutanol were added, 1.5 g of a 10% aqueous solution of sodium propionate was then added, and the resulting mixture was adjusted to pH 6 to 7 with acetic acid. This was adjusted with isobutanol to a nonvolatile content of 17% as measured by JIS K-6833 and ripened for 5 days at room temperature. The resulting colloidal silica-laden organopolysiloxane composition had a viscosity of about 5 centistokes and the nonvolatile component had a number average molecular weight of about 1,000.

[0094]

[Synthesis Example 10]

The procedure of Synthesis Example 9 was repeated except that 3.0 g of a 10% aqueous solution of tetramethylammonium benzoate was used instead of the sodium propionate aqueous solution, obtaining a colloidal silica-laden organopolysiloxane composition.

[0095]

[Synthesis Example 11]

The procedure of Synthesis Example 10 was repeated except that there was further added 1.8 g of 2,2',4,4'-tetrahydroxybenzophenone (corresponding to 2 parts per 100 parts of the solids of the colloidal silica-laden organopolysiloxane composition), obtaining a colloidal silica-laden organopolysiloxane composition.

[0096]

<Synthesis of silyl-modified photo-stabilizer>

[Synthesis Example 12]

A 0.3-liter flask equipped with a stirrer, condenser and thermometer was charged with 100 g (0.5 mol) of 2,2,6,6-tetramethyl-4-allyl-piperidine and 0.13 g of a butanol solution of chloroplatinic acid (2% solution of

H₂PtCl₆·6H₂O). To the flask at room temperature, 80.6 g (0.66 mol) of trimethoxysilane was added dropwise over one hour, and reaction effected at 90°C for 5 hours. At the end of reaction, distillation was effected under vacuum, collecting
5 126 g of a fraction at 151-154°C at 7 mmHg. By gas chromatography, 2,2,6,6-tetramethylpiperidino-4-propyltrimethoxysilane was collected at a purity of 97%. Its structure was confirmed by IR spectrometry and
10 proton-NMR analysis.

[0097]

Examples of the invention are given below by way of illustration. The abbreviations for UV-absorbers, hindered amine photo-stabilizers, and organic copolymers used in Examples and Comparative Examples have the following
15 meaning.

[0098]

<UV-absorbers>

- UVA-1: reaction product of Synthesis Example 1
- UVA-2: reaction product of Synthesis Example 2
- 20 UVA-3: reaction product of Synthesis Example 3
- UVA-4: reaction product of Synthesis Example 4
- UVA-5: 2,2',4,4'-tetrahydroxybenzophenone
- UVA-6: 2,4-dihydroxybenzophenone
- UVA-7: 2-(3,5-di-t-butyl-2-hydroxyphenyl)-5-chlorobenzo-
25 triazole
- UVA-8: 2-(2-hydroxy-4-hexyloxyphenyl)-4,6-diphenyltriazine
- UVA-9: a copolymer of 2-(2'-hydroxy-5'-methacryloxyethyl-phenyl)-2H-benzotriazole (30%) and methyl methacrylate (70%)
- 30 UVA-10: a copolymer of 2-(2'-hydroxy-5'-methacryloxyethyl-phenyl)-2H-benzotriazole (30%) and styrene (70%)

<Microparticulate inorganic oxides>

- UV-1: titanium oxide sol (20% methanol dispersion of TiO₂ with a mean particle size of 20 mμ)
- 35 UV-2: surface treated titanium oxide sol (20% methanol dispersion of titania particles surface coated with

SiO₂, containing 85% TiO₂, and having a mean particle size of 20 mμ)

5 UV-3: microparticulate compound oxide sol (20% methanol dispersion of mixed compound titanium oxide having an average composition: TiO₂/ZrO₂/SiO₂ = 70/8/22 and having a mean particle size of 20 mμ)

UV-4: cerium oxide sol (20% methanol dispersion of CeO₂ with a mean particle size of 20 mμ)

10 UV-5: surface treated zinc oxide sol (20% methanol dispersion of zinc oxide particles surface treated with 15% silica and having a mean particle size of 20 mμ)

UV-6: silica sol (20% methanol dispersion of SiO₂ with a mean particle size of 20 mμ)

<Hindered amine photo-stabilizers>

15 HALS-1: N-acetyl-3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidiny)pyrrolidine-2,5-dione

HALS-2: a condensate of 1,2,3,4-butanetetracarboxylic acid, 2,2,6,6-tetramethyl-piperidinol and tridecanol

20 HALS-3: 2,2,6,6-tetramethylpiperidino-4-propyltrimethoxy-silane synthesized in Synthesis Example 12

<Alkoxysilyl group-containing organic copolymers>

Pol-1: the reaction product of Synthetic Example 5

Pol-2: the reaction product of Synthetic Example 6

Pol-3: the reaction product of Synthetic Example 7

25 <Compounds containing nitrogen and alkoxysilyl group in molecule>

NSi-1: ureidopropyltriethoxysilane

NSi-2: the reaction product of Synthetic Example 8

<Colloidal silica-laden organopolysiloxane compositions>

30 HC-1: colloidal silica-laden organopolysiloxane composition of Synthetic Example 9

HC-2: colloidal silica-laden organopolysiloxane composition of Synthetic Example 10

HC-3: colloidal silica-laden organopolysiloxane composition of Synthetic Example 11

[0099]

In Examples, physical properties were measured and rated by the following procedures.

(1) Weathering test

5 An accelerated weathering test was carried out by a carbon arc sunshine weatherometer according to JIS K-5400. After 5,000 hours, a yellowing factor and adhesion were examined according to JIS K-7103. Those samples having a yellowing factor of up to 7 and good adhesion were rated
10 "Passed."

(2) Marring test

 Using a Taber abrader equipped with an abrasive wheel CS-10F, a sample was rotated under a load of 500 g according to ASTM 1044. After 1,000 revolutions, the sample was
15 measured for haze. A Taber abrasion (%) was calculated as the haze after test minus the haze prior to test.

(3) Adhesion of cured film

 An adhesive tape test was carried out according to JIS K-5400 by scribing a sample with a razor along eleven spaced
20 1-mm apart orthogonal lines to define 100 square sections in the coating, closely applying a commercially available adhesive tape thereto, and quickly peeling the adhesive tape by an angle of 90 degrees. The number (X) of remaining (not peeled) coating sections is expressed as X/100.

25 [0100]

[Examples and Comparative Examples]

(1) Preparation of primer coating composition

 Primer coating compositions (a) to (z) were prepared according to the formulation shown in Tables 1 to 3 by
30 mixing the organic copolymer (Pol-1 to 3) prepared in Synthetic Examples 5 to 7, polymethyl methacrylate having an average molecular weight of 150,000, the compound containing nitrogen and alkoxysilyl group in molecule (NSi-1, 2), the silyl-modified UV-absorber (UVA-1 to 4) prepared in
35 Synthetic Examples 1 to 4, the UV-absorber (UVA-5 to 10), and the photo-stabilizer (HALS-1 to 3), and diluting the mixture with a 20/80 mixture of diacetone alcohol and

ethylene glycol monomethyl ether to a concentration of 10% organic copolymer solids.

[0101]

(2) Preparation of coating composition

5 Coating compositions (A) to (Z) were prepared according to the formulation shown in Tables 4 to 6 by mixing the colloidal silica-laden organopolysiloxane composition (HC-1 to 3) prepared in Synthetic Examples 9 to 11, the silyl-modified UV-absorber (UVA-1 to 4) prepared in
10 Synthetic Examples 1 to 4, the UV-absorber (UVA-5 to 10), and the microparticulate inorganic oxide (UV-1 to 6).

[0102]

 It is noted that the following procedure was employed when the silyl-modified UV-absorber was incorporated in the
15 colloidal silica-laden organopolysiloxane composition from the first. The resulting compositions are designated UVA-11 to 14. In these cases, HC-1 to 3 were not separately used.

[0103]

Preparation procedure

20 A 1.0-liter flask equipped with a stirrer, condenser and thermometer was charged with 164 g of methyltriethoxysilane, 19.7 g of UVA-1, and 46 g of isobutanol, which were maintained below 5°C under ice cooling while stirring. To the flask, 138 g of
25 water-dispersed colloidal silica (containing 20% of SiO₂) below 5°C was added. The contents were stirred for 2 hours under ice cooling and for 8 hours at 20 to 25°C, following which 45 g of diacetone alcohol and 50 g of isobutanol were added. Thereafter, 1.5 g of a 10% aqueous solution of
30 sodium propionate was added to the reaction solution, which was adjusted to pH 6 to 7 with acetic acid. This was diluted with isobutanol so as to give a nonvolatile concentration of 19% as measured according to JIS K-6833. Ripening for 5 days at room temperature yielded a silane
35 hydrolyzate solution having a viscosity of about 5 centistokes and the nonvolatile matter had a number average molecular weight of about 1,000. This is designated UVA-11.

- UVA-12 was prepared by substituting UVA-2 for UVA-1.
- UVA-13 was prepared by substituting UVA-3 for UVA-1.
- UVA-14 was prepared by substituting UVA-4 for UVA-1.

[0104]

5 (3) Preparation of surface-coated part

The primer coating composition, if used, was applied onto a cleaned surface of a polycarbonate resin sheet of 0.5 mm thick by the flow coating method and cured at about 120°C for about 30 minutes, obtaining a cured primer coating of 2
10 to 5 μ m thick. The colloidal silica-laden organopolysiloxane coating composition obtained in above (2) was applied onto the primer coating by the flow coating method and cured at about 120°C for about one hour, obtaining a cured coating of 2 to 5 μ m thick. In the event of omitting the primer, the
15 colloidal silica-laden organopolysiloxane coating composition was applied onto a cleaned surface of a polycarbonate resin sheet of 0.5 mm thick by the flow coating method and cured at about 120°C for about one hour, obtaining a cured coating of 2 to 5 μ m thick. The thus
20 surface-coated sheets were examined for physical properties, with the results shown in Table 7.

[0105]

Table 1

	Primer coating composition (Examples)								
Primer designation	a	b	c	d	e	f	g	h	i
UVA	UVA-1 (20 parts)	UVA-1 (30 parts)	UVA-1 (40 parts)	UVA-2 (30 parts)	UVA-3 (30 parts)	UVA-4 (30 parts)	UVA-1 (30 parts)	UVA-1 (30 parts)	UVA-1 (30 parts)
Organic copolymer	Pol-1 (100 parts)	Pol-1 (100 parts)	Pol-1 (100 parts)	Pol-2 (100 parts)	Pol-3 (100 parts)	Pol-1 (100 parts)	Pol-1 (100 parts)	Pol-1 (100 parts)	Pol-1 (100 parts)
Polymethyl methacrylate	-	-	-	-	-	-	20 parts	20 parts	20 parts
Nsi	-	-	-	-	-	-	-	NSi-1 (5 parts)	NSi-2 (20 parts)
HALS	-	-	-	-	-	-	-	-	HALS-1 (10 parts)

5

[0106]

Table 2

	Primer coating composition (Examples)							
Primer designation	j	k	l	m	n	o	p	q
UVA	UVA-1 (30 parts)	UVA-1 (30 parts)	UVA-1 (30 parts)	UVA-1 (27 parts) + UVA-5 (3 parts)	UVA-1 (27 parts) + UVA-7 (3 parts)	UVA-1 (27 parts) + UVA-8 (3 parts)	UVA-1 (27 parts) + UVA-9 (3 parts)	UVA-1 (27 parts) + UVA-10 (3 parts)
Organic copolymer	Pol-1 (100 parts)	Pol-1 (100 parts)	Pol-2 (100 parts)	Pol-1 (100 parts)	Pol-1 (100 parts)	Pol-1 (100 parts)	Pol-1 (100 parts)	Pol-1 (100 parts)
Polymethyl methacrylate	20 parts	20 parts	20 parts	-	-	-	20 parts	-
Nsi	NSi-1 (5 parts)	NSi-2 (20 parts)	NSi-2 (30 parts)	NSi-2 (20 parts)	NSi-2 (20 parts)	NSi-2 (20 parts)	NSi-2 (20 parts)	NSi-2 (20 parts)
HALS	HALS-2 (10 parts)	HALS-3 (6 parts)	HALS-3 (6 parts)	HALS-1 (3 parts)	HALS-3 (10 parts)	HALS-3 (6 parts)	HALS-1 (2 parts)	HALS-1 (2 parts)

[0109]

Table 5

	Coating composition (Examples)							
Coating composition designation	J	K	L	M	N	O	P	Q
Colloidal silica-laden organopolysiloxane (as solids)	HC-1 (100 parts)	HC-1 (100 parts)	HC-1 (100 parts)	HC-1 (100 parts)	-	-	-	-
UVA	UVA-1 (10 parts)	UVA-1 (10 parts)	UVA-1 (30 parts)	UVA-1 (10 parts)	UVA-11 (100 parts)	UVA-12 (100 parts)	UVA-13 (100 parts)	UVA-14 (100 parts)
UV	UV-5 (20 parts)	UV-6 (20 parts)	-	-	-	-	-	-
HALS	-	-	-	HALS-3 (3 parts)	-	-	-	-

5

[0110]

Table 6

[illegible]

[0111]

Table 7

	Primer	Coating composition	Initial		Weathering	
			Yellowing factor	Taber abrasion	Yellowing factor	Adhesion
Example 1	a	A	1.0	7	1.5	100/100
Example 2	b	B	1.2	7	2.0	100/100
Example 3	c	C	1.2	7	2.5	100/100
Example 4	d	D	1.0	7	2.0	100/100
Example 5	e	E	1.4	8	2.5	100/100
Example 6	f	F	1.4	7	3.0	100/100
Example 7	g	G	1.0	8	2.5	100/100
Example 8	h	H	1.0	8	2.5	100/100
Example 9	i	I	1.0	7	2.0	100/100
Example 10	j	J	1.0	8	2.0	100/100
Example 11	k	K	1.5	7	2.5	100/100
Example 12	l	L	1.5	8	2.0	100/100
Example 13	m	M	1.5	9	3.0	100/100
Example 14	n	N	1.5	9	3.0	100/100
Example 15	o	O	1.2	9	3.0	100/100
Example 16	p	P	1.2	9	3.0	100/100
Example 17	q	Q	1.2	9	3.0	100/100
Example 18	-	A	1.0	8	2.5	100/100
Example 19	-	F	1.0	8	2.5	100/100
Example 20	-	I	1.0	8	2.0	100/100
Example 21	-	M	1.0	9	1.5	100/100
Example 22	-	N	1.0	8	1.5	100/100
Example 23	a	HC-1	1.0	8	1.5	100/100
Example 24	c	HC-3	1.2	8	2.0	100/100
Example 25	j	HC-1	1.0	9	1.5	100/100
Example 26	l	HC-3	1.0	8	2.0	100/100
Example 27	m	HC-3	1.0	7	1.5	100/100
Comparative Example 1	r	R	3.5	10	15	0/100
Comparative Example 2	s	S	7.5	15	30	0/100
Comparative Example 3	t	T	2.5	15	10	0/100
Comparative Example 4	u	U	5.0	20	35	0/100
Comparative Example 5	v	V	2.0	15	10	50/100
Comparative Example 6	w	W	2.0	15	10	50/100
Comparative Example 7	x	X	2.0	20	10	50/100
Comparative Example 8	y	Y	2.0	20	10	50/100
Comparative Example 9	z	Z	8.0	15	30	0/100
Comparative Example 10	-	X	9.0	20	25	0/100
Comparative Example 11	s	HC-1	2.0	10	20	50/100
Comparative Example 12	w	HC-3	2.0	10	25	0/100
Comparative Example 13	z	HC-1	2.0	10	20	50/100

[0112]

[Effect of the Invention]

Coated plastic articles, especially of polycarbonate resins, having coatings of the inventive coating
5 compositions are endowed with improved transparency, mar resistance, weather resistance and chemical resistance. They are suited on outdoor use, for example, as windows and windshields on automobiles, aircraft and other transporting vehicles, building windows, and acoustic barrier walls along
10 highways.



2000-027713

[ABSTRACT]

[Means for Solution]

5 A coating composition comprising the reaction product of
a benzotriazole compound having a polymerizable vinyl group and
a hydroxyl group with a silane compound and/or a (partial)
hydrolyzate thereof.

[Effect]

10 Coated plastic articles, especially of polycarbonate resins,
having coatings of the inventive coating compositions are endowed
with improved transparency, mar resistance, weather resistance
and chemical resistance. They are suited on outdoor use, for
example, as windows and windshields on automobiles, aircraft and
other transporting vehicles, building windows, and acoustic
15 barrier walls along highways.

[Selected Drawing] none